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DEVELOPING METHODS FOR ANALYZING OIL DISPERSANTS IN SEAWATER

by

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16. ABSTRACT

An analytical method was sought for determining the concentrations of dispersants in seawater contaminated with oil in both field and laboratory situations.

Methods of analysis for surfactants found in the literature included spectrophotometry, gas chromatography (GC), thin-layer chromatography (TLC), and high performance liquid chromatography (HPLC). References to collection, concentration, and cleanup methods included liquid/liquid extractions, gas stripping, and solid sorbents.

Of seven dispersants tested, one contained solely anionic surfactants, three contained only nonionic, and three contained both anionic and nonionic surfactants.

HPLC normal phase, reverse phase, and ion exchange column techniques were tried. Detection methods included (1) direct measurement of the surfactants by tensammetry and ultraviolet (UV) spectrometry, and (2) derivation of the surfactant with phenyl isocyanate with subsequent measurement by UV spectrometry. The most promising method of those tested was analysis of the phenyl isocyanate derivative of POE nonylphenol by normal phase HPLC using UV spectrometric detection.

A method of collection, concentration, and cleanup of seawater solutions of dispersants containing oil was developed using the solid sorbent SEP-PAK C_{18}* cartridge. This sorbent successfully removed compounds that interfered with colorimetric tests.

* Waters Association, Inc., trademark

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

This report describes research conducted to develop an analytic method for determining the concentration of dispersants in seawater contaminated with oil in both field and laboratory situations. The most promising method of those tested was analysis of the phenyl isocyanate derivative of POE nonylphenol by normal phase, high performance liquid chromatography using ultraviolet spectrometric detection. Also, a method was developed for collection, concentration, and cleanup of seawater solutions of dispersants containing oil using a commercially available, solid sorbent cartridge.

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Municipal Environmental Research
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ABSTRACT

Research was conducted to develop an analytical method for determining the concentrations of dispersants in seawater contaminated with oil in both field and laboratory situations.

The literature was reviewed, focusing on the physical and chemical properties of the surfactants that are used in oil dispersants and also on methods for the analysis, collection, concentration, cleanup, and preservation of trace quantities of these surfactants in marine environments. Methods of analysis for surfactants found in the literature included spectrophotometry, gas chromatography (GC), thin-layer chromatography (TLC), and high performance liquid chromatography (HPLC). Literature references to methods of collection, concentration, and cleanup include liquid/liquid extractions, gas stripping, and solid sorbents.

Seven commercially available dispersants were analyzed colorimetrically to determine the class of surfactants (ionic or nonionic) that they contained. Only one dispersant contained solely anionic surfactants. Of the six other dispersants tested, three contained only nonionic surfactants and the remaining three contained both anionic and nonionic surfactants.

Several instrumental methods of analysis were investigated, all of which used HPLC as the method for separation of the mixed surfactants. Normal phase, reverse phase, and ion exchange column techniques were tried. Detection methods included (1) direct measurement of the surfactants by tensammetry and ultraviolet (UV) spectrometry, and (2) derivation of the surfactant with phenyl isocyanate with subsequent measurement by UV spectrometry. The most promising method of those tested was analysis of the phenyl isocyanate derivative of POE nonylphenol by normal phase HPLC using UV spectrometric detection.

A method of collection, concentration, and cleanup of seawater solutions of dispersants containing oil was developed using the solid sorbent SEP-PAK C_{18}* cartridge. This sorbent successfully collected and concentrated surfactants from seawater containing dispersed oil. Recoveries of POE nonylphenol from collected samples were 100% under the conditions tested. Highly colored compounds in oil, which interfere in colorimetric tests, were removed by this sorbent.

This report was submitted in fulfillment of Grant No. R-807059-01 by SRI International under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period April 21, 1980, through April 30, 1982, and work was completed as of April 30, 1982.

*Waters Association, Inc., trademark

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SECTION 1

INTRODUCTION

The use of surface active agents (dispersants) to treat spilled oil is becoming more accepted. The surfactants are incorporated into a complex proprietary formulation that is applied to the oil spill either directly or after dilution with seawater. The wake of the boat and/or the natural mixing energy of the ocean causes the oil to disperse as fine droplets into the water column, where the larger surface area of the droplets promotes chemical and biological transformations of the oil.

Tests of dispersant effectiveness under actual field conditions have been performed in Canada and Great Britain for years, and more recently in the United States by the U.S. Environmental Protection Agency (EPA), and the Southern California Petroleum Contingency Organization. Laboratory tests of dispersant effectiveness and toxicity are also routinely made. In both field and laboratory tests, the dispersed oil in the water column can be extracted and quantitatively measured by spectrophotometry. However, no analytical methods currently exist for measuring the amount of dispersant product in the water column in either the presence or the absence of oil. Thus the concentration of dispersant in the water column after application to a spill cannot be measured. Also, the environmental fate of dispersion products has not been studied because the rate of disappearance by either dispersion or by chemical or biological transformation cannot be measured. Before these studies can be performed, analytical methods for the dispersant products must be developed.

Results of a literature survey (Appendix A) indicated that the following research areas should be selected and investigated:

(1) Ionic classification of dispersant products by colorimetric methods;

(2) Development and evaluation of several high performance liquid chromatography (HPLC) detection methods;

(3) Development and evaluation of several HPLC separation methods; and

(4) Evaluation of solid sorbents for collection of dispersant products in marine environments.

SECTION 2

CONCLUSIONS

The major active ingredients in oil dispersants were found to be anionic and nonionic surfactants. Of the seven commercially available oil dispersants tested, one contained anionic surfactants, three contained nonionic surfactants, and three contained both anionic and nonionic surfactants. No cationic surfactants were found in any of the four oil dispersants tested.

Tensammetry was investigated as a method for detecting oil dispersants. Our attempt at developing such a detection method was unsuccessful because of (1) the limited information on the use of tensammetry, (2) the complexity of the equipment and the sophistication of the technique, and (3) the high detection limits we experienced. Tensammetry may be used in limited analyses of surfactants, but it is much too complex and sophisticated for routine use.

A more practical approach is to derive the surfactants in oil dispersants and analyze them by existing HPLC detection methods such as UV detection. We have derived a polyoxyethylene (POE) nonionic surfactant with phenyl isocyanate, which increased its response by UV detection. Ion chromatography using a conductivity detector should be explored as a method for anionic surfactants.

Surfactants can be collected on solid sorbents. Both anionic and nonionic surfactants were successfully collected on SEP-PAK C_{18} cartridges (Waters Associates, Inc.). These cartridges could also be used to concentrate and isolate surfactants from potential interferences present in seawater and oil. Other solid sorbents such as XAD resins used in amounts larger than are available in the SEP-PAK C_{18} cartridges could be used to collect large-volume samples.

SECTION 3

RECOMMENDATIONS

Though several areas of investigation described in this report have produced promising results, further work is required for adequate development and validation of the methods of collection and analysis. The SEP-PAK C_{18} collection method needs further testing, and other sorbents should be investigated. The phenyl isocyanate derivation method of analysis needs more thorough testing, and a method for analysis of anionic surfactants needs to be developed.

The collection method using SEP-PAK C_{18} cartridges has been shown to collect, isolate, and concentrate several surfactants in the presence of seawater and oil. Further work is necessary to test this method with other surfactants and oil dispersants. Capacities for these surfactants and oil dispersants in the presence and absence of oils should be determined.

Other sorbents such as XAD resins (Rohm and Haas, Philadelphia, PA) have been successfully used in the collection of organics from water and should be tested for use in collecting surfactants. XAD resins are available in bulk and could be used for collecting surfactants from larger volumes of water than SEP-PAK C_{18} cartridges are capable of collecting. Simulated or actual field tests of these sorbents should be made after laboratory evaluation of their applicability to collections of surfactants from seawater containing oil.

The phenyl isocyanate derivation method combined with HPLC has shown promising results as a quantitative analytical method in our limited tests. More thorough testing of this method, including tests with varieties of nonionic surfactants and oil dispersants, is necessary. This method of analysis needs to be adapted for use with the sample collection method. Methanol has been used to elute surfactants from SEP-PAK C_{18}. However, because phenyl isocyanate reacts with alcohols, another solvent compatible with the derivation procedure must be found or methanol must be removed from the eluent before derivation.

A method of analysis is needed for anionic surfactants, which have been shown to be present in oil dispersants. Ion chromatography using a conductivity detector or reverse phase HPLC using ion pairing and UV detection are possible instrumental methods of analysis for anionics.

SECTION 4

RESULTS AND DISCUSSION

CLASSIFICATION OF SURFACTANTS IN OIL DISPERSANTS

Since no information was available on the composition of commercially available oil dispersants, an investigation was made to determine the types of surfactants used in these dispersants. Seven oil dispersants were tested using methyl orange[1], Azure A[1], and ammonium cobaltothiocyanate[2] colorimetric methods to determine the presence of cationic, anionic, and nonionic surfactants, respectively. Surfactant standards were also tested to determine the specificity of and interferences in each test. The detailed procedures of these colorimetric methods can be found in Appendix B. The dispersants and their manufacturers are listed in Appendix C. The results of these colorimetric analyses are presented in Table 1. Although these test are not exhaustive, they show that the oil dispersants tested contained primarily anionic and nonionic surfactants and no cationic surfactants. Test conducted with standard anionic and nonionic surfactants showed no positive interferences of anionics in nonionic tests and vice versa. In the case of tall oil fatty acids (an anionic surfactant), the Azure A analytical method for anionics was negative. Therefore, negative Azure A tests of the oil dispersants do not exclude tall oil fatty acids.

Since no evidence was found that oil dispersants contain cationic surfactants, only anionic and nonionic surfactants were studied in the development of sample collection and instrumental analytical methods for oil dispersants.

HPLC DETECTION AND SEPARATION METHODS

Several methods of analysis for oil dispersants, after collection and isolation from the seawater-oil matrix, were tested. After a review of the literature, HPLC was selected as the most promising analytical technique. Two detection methods for HPLC were tested: tensammetry, which is a form of polarography, and derivation of surfactants with ultraviolet (UV) absorbing groups for UV detection.* After all potential possibilities for tensammetric detection were exhausted, derivation was found to be the most promising analytical technique for detecting oil dispersants.

---

* The two commonly used LC detectors, UV and refractive index (RI), have several shortcomings for the detection of oil dispersants. Many dispersants contain only aliphatic surfactants, which have little, if any, UV absorption, and the sensitivity of the RI detector is not great enough.

TABLE 1. COLORIMETRIC ANALYSES OF OIL DISPERSANTS AND SURFACTANTS

	Methyl orange method for cationic surfactants (CS)	Azure A for anionic surfactants (AS)	Ammonium cobaltothiocyanate method for nonionic surfactants (NS)
Oil dispersants			
Corexit 9527*	-	+	+
Gold Crew*	-	+	+
Sea Master, NS-555*	-	-	+
BP-1100X*	-	-	+
Conco K*		-	+
Nokomis 3 Mi-Dee Formula 50*		+	+
AP*		+	-
Surfactant standards			
POE tallow amine (CS)	+		
Sodium lauryl sulfate (AS)		+	-
Tall oil fatty acids (AS)		-	-
Sodium n-dodecylbenzene sulfonate (AS)		+	-
Sodium petroleum sulfonate (AS)		+	
POE nonylphenol (NS)		-	+
Laurate of polyethylene glycol 400 (NS)		-	
POE sorbitan monolaurate (NS)		-	

*See Appendix C for complete identification.

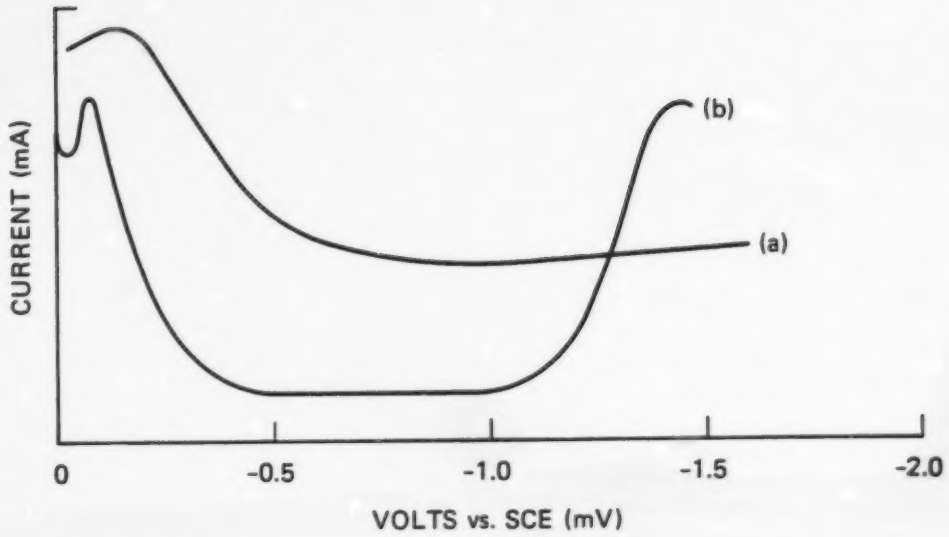
Direct current (dc) polarography measures the current through an electrolyte solution as a function of the potential applied between two electrodes (a reference and a working polarizable electrode) placed in solution.[3] Alternating current (ac) polarography measures the current produced when a small amplitude (10-30 mV peak-to-peak) sinusoidal potential is superposed on the dc potential.[4] If the chemical of interest undergoes oxidation or reduction at a certain dc potential, the current produced (Faradaic current) is usually 45° out of phase with the applied ac potential (the true phase depends on the redox kinetics). Tensammetry, which is a form of ac polarography, however, does not require the occurrence of a redox reaction for detection.[4] Instead, it measures the change in the capacitance of the electrical double layer surrounding the working electrode (dropping mercury electrode of DME) by measuring the current 90° out of phase with the ac potential (assuming no Faradaic current). The change in capacitance is caused by sorption and desorption of surfactants on the working electrode. Lankelma and Poppe found that the potential where the concentration of surfactant is proportional to a decrease in current over the widest range of concentrations is the valley between the two peaks (known as tensammetric peaks or waves) as shown in Figure 1.[5]

A method for using tensammetry as an HPLC effluent detector for surfactants has been presented by Lankelma and Poppe.[5] Because the sorbent system used by Lankelma and Poppe was unavailable, several attempts were made to find an HPLC solvent-sorbent system that would: (1) separate both ionic and nonionic surfactants, (2) contain enough supporting electrolyte in the solvent system to produce moderate to low cell resistances, (3) produce a significant difference in the cell current, at a certain potential, and surfactant solution. Separation procedures were tested using sodium n-dodecylbenzene sulfonate. Concentrations of sodium N-dodecylbenzene were high enough (100 ppm) that a UV detector could be used.

Two columns, a Waters μ-Bondapak C_{18} reverse phase column and a Whatman Partisil-10 SAX strong anion exchange column, were each tested with various solvent systems. One solvent system for the reverse phase column fulfilled the first criterion but not the third.[6]

A solvent system (see Appendix B) for the anion exchange column was found that fulfilled the first and third criteria, but not the second. The cell for tensammetric detection of the column effluent (see Appendix B) was assembled, and chromatograms were run. An injection of a 34-ppm solution of sodium n-dodecylbenzene sulfonate in water was made for these runs. Tensammetric detection of the solvent was easily achieved. However, at surfactant concentrations large enough for UV detection, the response of the tensammetric detector to the surfactants was barely distinguishable from the baseline. We varied the dead volume, mercury drop time, and dc potential to see if the surfactant could be detected, but the results were negative.

Several factors could have been responsible for our inability to achieve a working tensammetric detector. Low electrolyte concentrations and the unavailability of electrical equipment for filtering the drop noise could

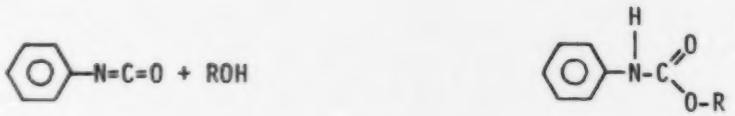


(a) Supporting electrolyte: p.10 M Na_2SO_4, 0.155 M acetic acid, 0.018 M sodium acetate.
(b) Supporting electrolyte and 108 ppm sodium dodecylbenzene sulfonate.

Figure 1. Tensammagram of n-dodecylbenzene solfonate.

have been responsible for our negative results. However, the sophisticated equipment required adds a high degree of complexity to this technique.

The technique presented by Allen and Linder[7] for determining the ethylene oxide oligomer distribution in nonionic surfactants using HPLC was then investigated and shown to be a promising technique for analyzing oil dispersants. This technique involved the derivation of alcohol ethoxylate surfactants with phenol isocyanate to give a urethane, a UV absorber.



Analysis is then made using HPLC with a normal phase column.

Since most commercial oil dispersants contain these types of surfactants, these dispersants would be expected to be susceptible to this derivation and analysis. Polyethoxylated nonylphenol, Corexit 9527, Conco K were derived neat with phenyl isocyanate and analyzed by the method of Allen and Linder.[7] Using a UV detector, we obtained a strong response for both POE nonylphenol and Corexit 9527 in the 2500 ppm range, as can be seen for POE nonlyphenol in Figure 2. The derivation was attempted in acetonitrile, but no response was obtained except for Conco K.

We were unable to fully evaluate this method for analysis because of the major emphasis on development of a tensammetric detector. However, initial results show that this method does work for the surfactants tested. Further tests are necessary to thoroughly evaluate this method.

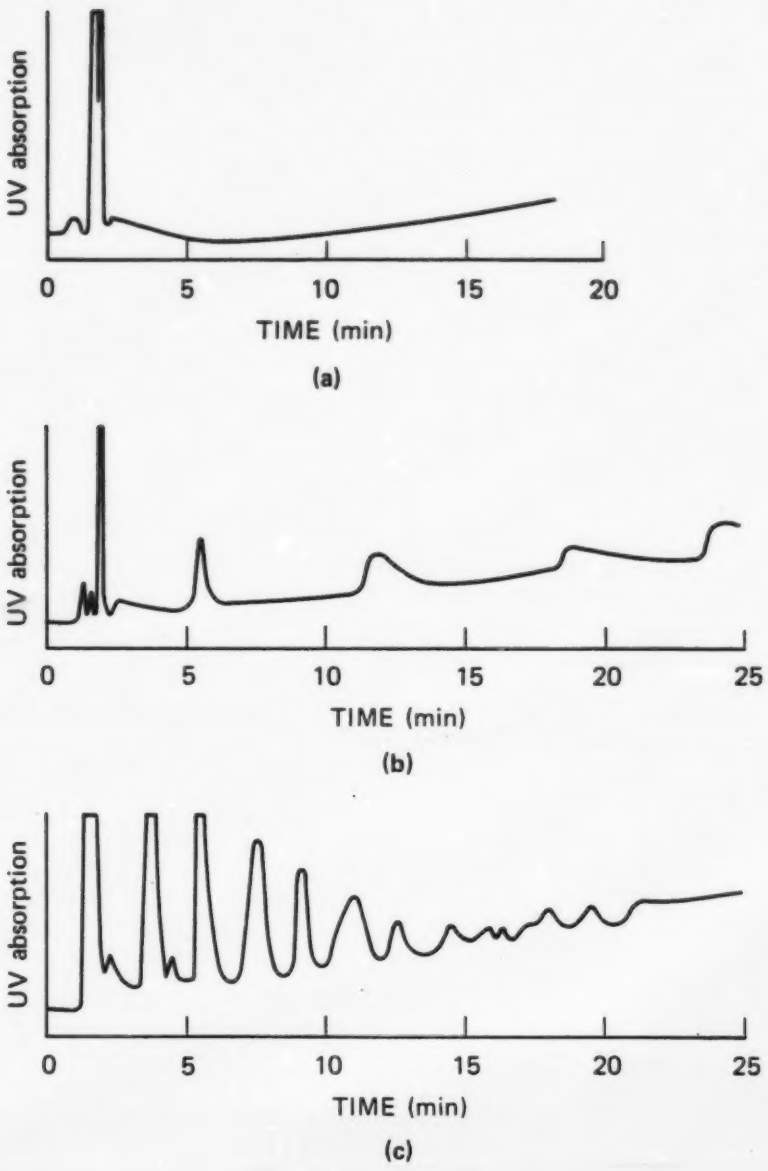


Figure 2. HPLC traces of (a) phenyl isocyanate, (b) underived POE nonylphenol, and (c) POE nonylphenol derived with phenyl isocyanate.

SAMPLE COLLECTION, CONCENTRATION, AND CLEANUP

One solid sorbent was successfully tested as a means of collecting, concentrating, and separating surfactants in oil dispersants from an oil-seawater matrix. The sorbent tested was a SEP-PAK C_{18} cartridge manufactured by Waters Associates, Inc., Milford, Massachusetts. The sorbent consists of a polymer cartridge filled with a reverse phase liquid chromatographic packing. The cartridge is made to fit syringe Luer end fittings. Samples and solvents are applied to the cartridge by syringe. The SEP-PAK C_{18} cartridge is used for collecting samples in a polar solvent, such as water. Polar compounds are not retained by the cartridge. The degree of retention of nonpolar compounds is a function of the polarity of the eluting solvent. Also, surface effects are important for the retention of the surfactants, especially ionic surfactants. Adsorbed organics are eluted with a less polar solvent.

This collection method was tested using standard surfactants in the presence and absence of seawater and oil. POE nonylphenol and sodium lauryl sulfate were used as representatives of nonionic and anionic surfactants, respectively. Methanol was used to elute the surfactants from the cartridge. The presence or absence of surfactant in the cartridge eluate tested was determined by colorimetric tests. The ammonium cobaltothiocyanate method was used for nonionics and the Azure A method for anionics. In both cases a blue extraction solvent indicated the presence of the nonionic or anionic surfactant, depending on the method used. The results of these tests are presented in Table 2.

Oil is the only interference in the nonionic surfactant colorimetric method. In the absence of oil and surfactants, neither methanol, methanol extracts of SEP-PAK C_{18}, nor seawater interfere in this method. The interfering components of the oil that absorb at 610 nm are retained on the SEP-PAK C_{18} and eluted with methanol are detected at 320 nm. Therefore, we have shown that a nonionic surfactant can be collected from a sample containing seawater and oil and detected colorimetrically without interference at 610 nm. Other nonionic surfactants and oil dispersants should be tested using a variety of crude oils to make sure that this method will work for a variety of surfactants and oils.

Both seawater and oil cause interferences in the anionic surfactant colorimetric analytical method. The interferences from seawater pass through the SEP-PAK C_{18} and are not eluted by methanol with the surfactants. Again, a wider variety of anionic surfactants and oils need to be tested to thoroughly validate this collection method.

Besides collecting and separating the surfactants from interferences, the SEP-PAK C_{18} cartridges can be used to concentrate samples whose concentration is too low for analysis. The tests whose results are shown in Table 2 were made using 100-ml samples containing about 10 ug ml^{-1} of surfactant and about 1500 $\mu g\ ml^{-1}$ light Arabian crude oil. Quantitative recoveries of the surfactants were achieved using three 2-ml methanol rinses of the SEP-PAK

Table 2. Evaluation of SEP-PAK C_{18} Cartridges as a Sorbent for Nonionic and Anionic Surfactant

Sample	Adsorbed by SEP-PAK C_{18}	Eluted with methanol
Oil* in freshwater	yes	no
Seawater salts	no	no
Oil* in seawater	yes	no
POE nonlyphenol in freshwater	yes	yes
POE nonylphenol in seawater	yes	yes
POE nonylphenol in seawater with oil*	yes	yes
Sodium lauryl sulfate in freshwater	yes	yes
Sodium lauryl sulfate in seawater with oil*	yes	yes

*Light Arabian crude oil

C_{18} cartridge, which represents a concentration of these samples by more than an order of magnitude. The maximum capacities for surfactants and crude oil have not been determined for SEP-PAK C_{18}. Collections of varying amounts of several surfactants and oil dispersants need to be made in the presence and absence of crude oil to determine the surfactant capacities of SEP-PAK C_{18}.

APPENDIX A

LITERATURE SEARCH

Before the literature search was begun, we made the following three assumptions about dispersant products applied to oil spills at sea:

(1) Dispersant products are complex mixtures of surfactants, buffers, modifiers, and carriers. Surfactants will be the primary substances to be collected and analyzed. Of these, nonionic and anionic surfactants are most prevalent. Cationic surfactants will not be considered in this study.

(2) Dispersant products will be present in an aqueous (seawater) matrix containing salts, petroleum products, biota, and other substances likely to interfere with sampling and analytical methods.

(3) Dispersant products are expected to be present in seawater at concentrations of at most 10 ppm.

The literature survey focused on physical and chemical properties and methods for the analysis, collection, concentration, cleanup, and preservation of trace quantities of surfactants in marine environments. The most relevant references are summarized in Tables A-1, A-2, and A-3 and are discussed below.

There was much information on the analysis of surfactants, especially by colorimetric methods. These methods are summarized in Table A-1, along with detection limits and known interferences. These methods involve complexation of the surfactant with a suitable reagent, extraction of the complexed surfactant into an organic phase, and colorimetric determination of the complex. Since the complexing reagent is frequently a metal complex, some methods use atomic absorption spectrophotometry (AA) for detection of the metal-surfactant complex. The colorimetric methods of analysis are generally sensitive and rapid and require minimal equipment. However, they are nonspecific and subject to interferences. Salts, especially Cl^- and certain metal ions, interfere. Most colorimetric methods are unsuitable for direct analysis of marine samples. Ocean waters may also contain natural surfactants that interfere. The Azure A, ammonium cobaltothiocyanate, and methyl orange methods listed in Table A-1 were used in our studies to characterize some commercial dispersants and to evaluate a solid sorbent collection method.

Less information was available on analytical methods based on chromatographic separation. Chromatographic methods offer the advantages of selectivity and the ability to separate interfering materials. It may be possible

TABLE A-1. SUMMARY OF SPECTROPHOTOMETRIC METHODS FOR THE ANALYSIS OF SURFACTANTS

Reagent	Reference	Class	Limit of detection (ppm)	Known interferences	Comments
Colorimetric methods					
Methylene blue	8, 9	Anionic	0.025	Organic sulfates, sulfonates, carboxylates, phosphates, and phenols; CN^-, Cl^-, NO_2, SCN^-	Requires 4-$CHCl_3$ extractions.
Azure A	2	Anionic	1	NO_3^-, HCO_3^-, SO_4^{2-}, SO_3^{2-}, Cl^-,	Author claims better suitability for seawater than methylene blue.
Copper(II)triethylenetetramine	10	Anionic	0.2	Metal ions (e.g., Ca^{2+}, Mn^{2+}) may interfere.	Complex is light sensitive.
Remacrylblau B Remacrylrot 2BL	11	Anionic	0.014		Single extraction gives 95% recovery; Cl^-, NO_3, etc., do not seriously interfere.
Phosphomolybdic acid	12, 13	Nonionic	0.5		Anionic surfactants and mineral salts do not interfere.
Dragendorf's reagent ($KBiI_4$ + $BaCl_2$)	14, 15	Nonionic	0.1	Alkaloids and many physiological substances	Surfactants may be precipitated or extracted in organic phase
Ammonium cobaltothiocyanate	1, 16	Nonionic	0.1		Alcohols & anionic surfactants do not seriously interfere.
Ferrocyanic acid	17	Nonionic	(Fairly high)	Sodium perborate	Lengthy procedure.
Sodium picrate	18	Nonionic	0.1	Anionic surfactants $\geq$0.2 ppm; cationic surfactants	
Methyl orange	2	Cationic	1		Anionic surfactants do not interfere.
Atomic absorption methods					
Bis(ethylenediamine)-Cu(11)	19	Anionic	0.0003	Organically bound Cu	Analysis as Cu by flameless AA.
K_2 [Zn(II)$(SCN)_4$]	20	Nonionic	0.05	S^{2-}, Fe^{3+}, Al^{3+}, Cr^{3+}; cationic surfactants	Analysis as Zn by AA.

to minimize cleanup procedures by use of chromatographic analysis and to determine anionic and nonionic surfactants simultaneously. However, these methods require more sophisticated equipment, generally in a well-equipped laboratory, and are time-consuming. These methods are summarized in Table A-2. Gas chromatography (GC) is usually not an appropriate method of analysis for surfactants. Ionic materials, and nonionic substances of high molecular weight, are generally not volatile enough for GC analysis. However, nonionic surfactants have been derived, which increases somewhat their vapor pressure or are analyzed by GC as their pyrolysis products.

Thin layer chromatography (TLC) and high performance liquid chromatography (HPLC) have been used to analyze all classes of surfactants. Published methods are limited and are mostly intended for quality control, not trace analysis. However, complex surfactant mixtures have been separated on normal phase, reverse phase, partition, and ion exchange columns. Therefore, HPLC appears to be the method of choice for separation and identification of dispersant products.

Detection after separation appears to be the limiting factor in TLC and HPLC methods. Standard methods of detection (UV absorbance, refraction index, electrochemical) are unsuitable for detection of small quantities of these products. A tensammetric HPLC detector has been described that responds specifically to surface active substances. This detector uses a modified ac polarograph. Substances that adsorb at the mercury-solution interface produce a change in the alternating current, giving rise to a signal. The authors[5] claim equivalent sensitivity to UV detectors, even for nonaromatic surfactants. The HPLC separation/tensammetric detection approach was the most promising method resulting from the literature survey, and the primary one we evaluated as an analytical method for dispersant products.

The literature survey also focused on methods to collect, concentrate, cleanup, and preserve samples of trace levels of surfactants. Extraction of surfactants into an organic phase has limited success. Surfactants are designed to collect at the water-oil interface and do not partition cleanly between phases. Wickbold[15] described an apparatus for stripping nonionic surfactants into an ethyl acetate phase by bubbling large quantities of nitrogen through the aqueous phase. This technique is effective, but it is time-consuming and unsuitable for field use.

There are indications that surfactants are more or less irreversibly sorbed on charcoal and silica gel, which would be unacceptable collection media. Several porous polymeric materials may be useful for concentrating trace levels and eliminating interferences. These are summarized in Table A-3. Amberlite XAD-2 and XAD-4 and open-pore polyurethane have been shown to retain certain surfactants. Ion exchange resins may also be useful in cleanup and concentration procedures. SEP-PAK C_{18} cartridges containing reverse phase HPLC packing were evaluated for the collection of surfactants. These cartridges were selected because they required a minimum of preparation and pretreatment.

TABLE A-2. SUMMARY OF CHROMATOGRAPHIC METHODS FOR THE ANALYSIS OF SURFACTANTS

Reference No.	Class	Detection limit	Stationary phase	Mobile phase	Detection	Comments
TLC methods						
21	Nonionic	0.2 ppm	Not stated (silica)	Acetone/water	Transmission photometry, developed with I vapors	Abstract only; performed in seawater.
22	Nonionic	Not stated	Silica gel	Chloroform/ methanol water	Dragendorf's reagent	Abstract only.
HPLC methods						
23	Anionic	Not stated	Amberlite GC-50 (weakly basic cation exchange)	Isopropanol/0.2 N NaCl	Collection of fractions and titration	Isopropanol necessary to keep surfactants in solution.
24	Cationic	Not stated	Amberlite GC-4B (weakly basic anion exchange)	Methanol/0.5 N NaCl	Collection of fractions and titration	Methanol necessary to keep surfactants in solution.
25	Anionic	Not stated (high)	μ-Bondapak C_{18} (reverse phase)	Methanol/water/ acetic acid	RI	
26	Anionic	<3 ppm	Licrosorb Si 60-ODS	Methanol/water + $(CTMA)_2^+ SO_2^{2-}$	UV at 223 nm	Paired ion chromatography. Samples preconcentrated on XAD-4.
5	Anionic, nonionic	<1 ppm	Tricresolphosphate (ion exchange)	0.1 M NA_2SO_4 + 0.03 M NaOAc + 0.16 M CH_3 COOH	Tensammeter	Paper describes in detail tensammetric detector.
27	Nonionic	Not stated (high)	Separon 40-S (semi-prep reverse phase	Methanol/water	RI	Method for polyethylene glycol derivatives
28	Nonionic	0.05 ppm	Styragel (styrene-divinylbenzene molecular sieve	Chloroform/hexane	IR	Paper details extensive cleanup procedures for oil and surfactants in water.
*	Nonionic	High	Zorbax-CN (medium polarity normal phase)	Heptane	UV at 278 nm	Method for ethoxylated nonylphenols.
29	Anionic	High	Amberlite XAD-2	Acetonitrile/ water + tetra-alkyl ammonium salts	UV at 254 nm	Evaluation of retention on XAD-2 as function of counter ion.

*Alan C. Hayman, E.I. du Pont de Nemours & Co., Wilmington, Delaware, private communication.

TABLE A-3. SUMMARY OF ADSORPTION MEDIA FOR SURFACTANTS

Adsorption medium	Reference	Class	Method/comments
Amberlite XAD-1	30	Anionic, cationic, & nonionic	Seawater acidified to pH 2, filtered through 0.5-μm filter; eluted with ethanol. XAD-1 did not retain carbohydrates, amino acids, proteins, or phenols.
Amberlite XAD-4	26	Anionic	Samples acidified to pH 2, eluted with methanol. Neutral solution resulted in poor retention.
Amberlite XAD-4	31	Nonionic	Eluted with acetone. Polyethylene glycols of MW <300 were not efficiently retained.
Open-pore polyurethane	32	Anionic	Eluted with methanol. Authors report greater capacity than XAD-4.

APPENDIX B

EXPERIMENTAL PROCEDURES*

COLORIMETRIC METHODS

The Azure A, methyl orange, and ammonium cobaltothiocyanate methods were used to measure anionic and polyoxyethylenated nonionic surfactants, respectively, in surfactant standards and commercial oil dispersants.

AZURE A METHOD[1]

The following reagents, equipment, and procedures were used for this colorimetric method. Reagent grade chemicals should be used.

Azure A Reagent--Dissolve 400 mg Azure A in 500 ml distilled H_2O containing 5 ml of 1.0 N sulfuric acid. Dilute to 1 liter with distilled water.

Stock Anionic Surfactant Solution--Weigh out 1.000 g. of the surfactant and dissolve it in 1 liter of distilled water.

Standard Anionic Surfactant Solution--Dilute 50.00 ml of the stock solution to 1 liter with distilled water.

Buffer Solution--Prepare an aqueous solution containing 0.25 M citric acid and 0.1 M disodium hydrogen orthophosphate.

Extracting Solvent--Chloroform.

Equipment-- Spectrophotometer capable of measuring absorbances at 623 nm, 250-ml separatory funnels, assorted graduate cylinders, assorted pipets, filter funnels (65mm), 1-liter volumetric flasks, glass wool, and 1-cm path length cuvettes.

Procedure--Pipet the water sample into a separatory funnel. Dilute with distilled water to 50 ml if water sample volume is less than 50 ml. Add 1 ml of Azure A reagent and 5 ml of the buffer solution. Mix well, then add 25.0 ml of chloroform and shake vigorously for 30 seconds. Allow the water and chloroform layers to separate, then filter the chloroform layer through a glass-wool-plugged funnel into a 1 cm path length cuvette. Measure the absorbance of the chloroform solution at 623 nm. Determine the

*All surfactant standards referred to in this report were reagent grade and obtained from Chem Services, Media, PA.

concentration of the anionic surfactant from a previously prepared calibration curve of that same surfactant. Qualitatively, a clear colorless chloroform layer indicates that little or no anionic surfactant is present, and a clear blue chloroform layer indicates that anionic surfactant(s) are present.

Interferences--Inorganic and organic anions give a positive test.

Limit of Detection--1 ppm of anionic surfactant.

METHYL ORANGE METHOD[1]

The reagents, equipment, and procedures used in this method of analysis are listed below.

Methyl Orange Reagent--Dissolve 0.10 g of methyl orange powder in a small amount of distilled water. Dilute to 100 ml or a concentration of 0.1% by weight.

Buffer Solution--Prepare an aqueous solution containing 0.25 M citric acid and 0.1 M disodium hydrogen orthophosphate.

Extracting Solvent--Chloroform.

Equipment--Spectrometer capable of measuring absorbance at 415 nm, 250-ml separatory funnels, assorted graduate cylinders, assorted pipets, filter funnels (65 mm), 100-ml volumetric flask, glass wool, and 1-cm path length cuvettes.

Procedure--Pipet an aliquot of the water sample into a separatory funnel and dilute to 50 ml with distilled water. Add 1 ml of the methyl orange reagent and 5 ml of the buffer solution. Mix well, then add 25 ml of chloroform and shake for 30 seconds. Allow the layers to separate (about 20 minutes) then filter the chloroform layer through a glass-wool-plugged funnel into a 1-cm path length cuvette. Measure the absorbance of the chloroform solution at 415 nm. A yellow chloroform layer indicates the presence of cationic surfactant(s).

Limit of Detection--1 ppm of cationic surfactant.

AMMONIUM COBALTOTHIOCYANATE METHOD[2]

Reagents, equipment, and procedures used for this method of analysis are described below. Reagent grade chemicals should be used.

Ammonium Cobaltothiocyanate Reagent--Dissolve 120 g of ammonium thiocyanate and 380 g of cobalt nitrate in distilled water and dilute to 1 liter. Extract twice with toluene to remove interferences.

Sodium Chloride--Reagent Grade.

Extraction Solvent--Toluene.

Equipment--Separatory funnels, 250 ml, assorted graduate cylinders, and pipets, filter funnels, glass wool, spectrometer capable of absorption measurements at 320 and 610 nm, and 1-cm path length cuvette.

Procedure--Pipet 100 ml of water sample into a 250-ml separatory funnel. Add 15 ml of the ammonium cobaltothiocyanate reagent and 30 g of the sodium chloride to the sample. Mix until all the sodium chloride is dissolved. Add 25.0 ml of toluene and shake vigorously for one minute. Allow the toluene and water layers to separate, then discard the water layer. Filter the toluene layer through a glass-wool-plugged filter funnel into a 1-cm path length curette. Measure the toluene solution at 320 or 610 nm. If oil or other UV-absorbing compounds are present in the water sample, 610 nm should be used. The method is less sensitive at 610 nm, but is less subject to interference than 320 nm. The concentration of polyethoxylated nonionics can be determined from a previously prepared calibration curve of the same presence of a polyethoxylated nonionic surfactant. A blue toluene layer indicates the presence of a polyethoxylated nonionic surfactant. A clear colorless toluene layer indicates that the polyethoxylated nonionic contains less than 3 polyethoxylate groups per molecule, or that the amount present is below the lower limit of the test, or that none is present.

Interferences--Polypropylbenzene sulfonate, n-alkyl sulfates, quarternary ammonium compounds, and polyethylene glycols interfere with this test. A mixed ion exchange resin can be used to remove cationic and anionic interferences.

Limit of Detection--0.1 ppm of nonionic surfactant.

TENSAMMETRIC DETECTION OF SURFACTANTS[5]

Reagents, equipment, and procedures used for this method of analysis are described below. Reagent grade chemicals should be used.

Eluting Solvent--Dissolve 0.499 g of sodium acetate trihydrate, 1.2 ml of glacial acetic acid, and 0.284 g of anhydrous sodium sulfate in enough Milli-Q water to make a 1-liter solution. Filter the solution through a 0.45-μm HA-type Milli-Pore filter.

Anionic Surfactant--Chem Service, sodium n-dodecylbenzene sulfonate.

Equipment--A Spectra-Physics 3500B, with a 1.0-ml sampling loop, and a Whatman Partisil-10 SAX column. A Princeton Applied Research PAR 174/70 drop timer was used with a gravity fed dropping mercury electrode (DME), a saturated calomel reference electrode (SCE), and a platinum counter electrode. A PAR 174A polarographic analyzer, PAR 174/50 interface, and a PAR 124A lock-in amplifier were also used for tensammetric measurement. Figure B-1 shows how the above equipment was connected.

Procedure--Inject 100-ppm samples of sodium n-dodecylbenzene sulfonate in water into the LC through the sampling loop. Direct the column effluent (flow rate of 0.52 ml min^{-1}) to the tip of the DME (see figure B-2) (~1-2 mm

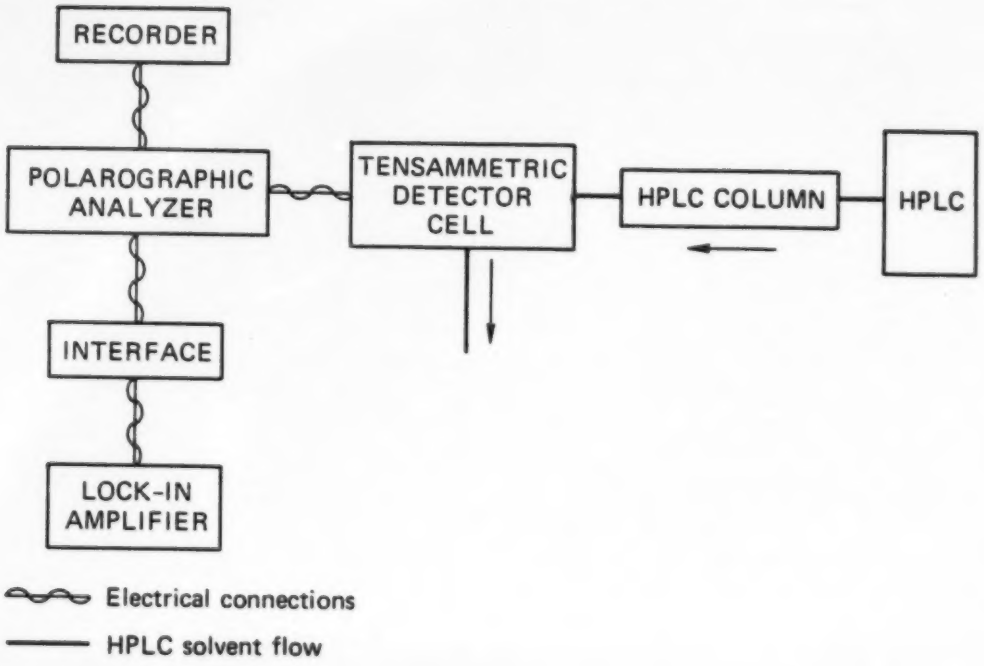


Figure B-1. Block diagram of the HPLC tensammetric detection system.

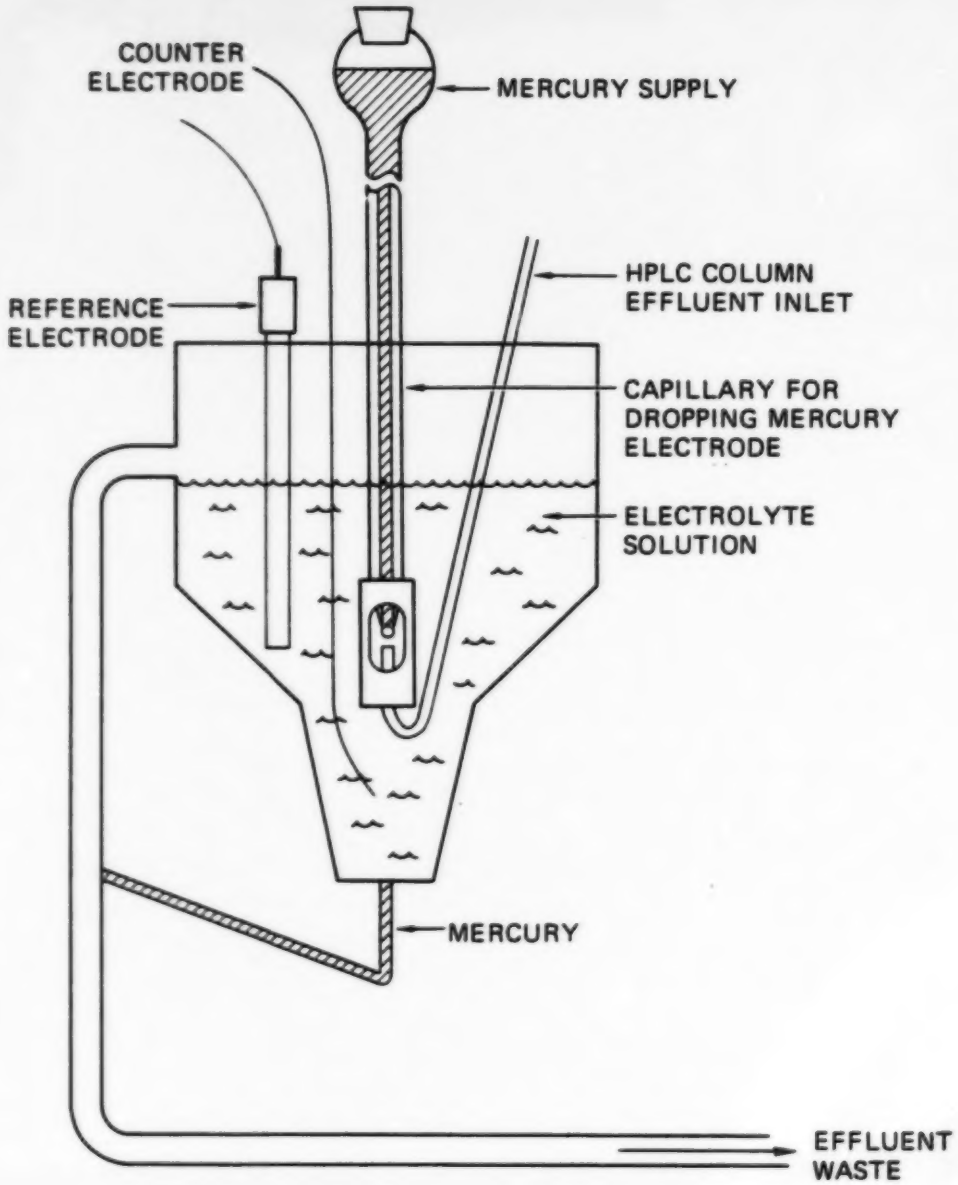


Figure B-2. Tensammetric detector cell.

distance between the tip of the DME and effluent outlet). The drop timer then dislodges a drop from the DME (both 1 s/drop and 0.5 s/drop were tried), and the measured current is directed to the polarographic analyzer, which controls the applied dc potential (both -500 mV and -800 mV relative to SCE were tried). The lock-in amplifier provides an ac potential of 10 mV peak-to-peak at 50 Hz, for superposition on the dc potential. Adjust the lock-in amplifier to detect the cell current 90° out of phase with the ac potential.

HPLC ANALYSIS BY DERIVATION[7]

Reagents, equipment, and procedures used for this method of analysis are described below.

Eluting Solvents--Filter Burdick and Jackson dichloromethane and Fisher HPLC grade methanol through 0.5-μm type FH Milli-Pore filters and degas before use.

Reagents--Surfactant Standard--Chem Service POE nonylphenol.

Oil Dispersants--Corexit 9527 and Conco K. Eastman Kodak phenyl isocyanate was used as the deriving agent.

Equipment--A Spectra-Physics 3500B, modified by removal of the mechanical mixer, with the 100-μl sampling loop, and a Waters μ-Portasil normal phase column. A Spectra-Physics 8200 UV detector was also used.

Procedure--Add approximately 10 μl of phenyl isocyanate to approximately 10 mg of surfactant in a lightly stoppered test tube. Heat the mixture to 50-60°C for 30 minutes. Allow the mixutre to cool to room temperature and dilute with 4 ml of dichloromethane and 1% methanol. A 2500-ppm sample results.

Analyze the 2500 ppm sample of the derived surfactants by HPLC, using a solvent of 99% dichloromethane and 1% methanol to 89% dichloromethane and 11% methanol in one hour (eluting solvent flow rate of 2 ml min^{-1}).

SURFACTANT COLLECTION METHOD

The following reagents and equipment were used in the collection and subsequent elution of the surfactants studied in this work.

Solvent--Use Water's SEP-PAK C_{18} cartridges to collect, concentrate, and separate the surfactants. Rinse each cartridge three times with 2-ml portions of methanol followed by three 2-ml rinses of water.

Methanol--Reagent grade.

Syringe--A syringe whose capacity will accomodate the water sample and a 10-ml syringe for rinsing cartridges.

Procedure--Place a seawater sample containing surfactants and oil in a syringe with a cleaned SEP-PAK C_{18} cartridge attached. Slowly force the sample through the cartridge. Rinse the cartridge with three 2-ml portions of purified freshwater. The cartridge can now be capped and stored for later extraction, or the surfactant can be immediately eluted with three 2 ml portions of methanol. Dilute the methanol extracts to the appropriate volumes with water and analyze.

Solvent Capacity--The surfactant capacity of the cartridges have not been determined. The greater the amount of oil and other strongly sorbed substances, the lower the surfactant capacity will be.

APPENDIX C

OIL DISPERSANT PRODUCT SOURCES

Dispersant	Manufacturer
Corexit 9527	Exxon Chemical Co.
Cold Crew	Ara Chem, Inc. 808 Gable Way El Cajon, CA
Sea Master, NS-555	Whale Chemical Co. 58 Winant Street Staten Island, NY
BP-1100X	BP North America 620 Fifth Avenue New York, NY
Conco K	Continental Chemical Co. 270 Clifton Blvd. Clifton, NJ 07015
Nokomis 3 Mi-Dee Formula 50	Nokomis International, Inc. Hayward, CA 94545
AP	Atlantic-Pacific Co.

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